MOSSBAUER STUDY OF HYPERFINE FIELD DISTRIBUTIONS AND SPIN CANTING IN LITHIUM-ZINC FERRITES

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ABSTRACT

In a Mössbauer study of the system $Li_{0.5-x/2}Zn_xFe_{2.5-x/2}O_4$ at 4.2K and in fields up to 70 kOe the occurrence of hyperfine field HF distributions at the Fe^{3+} ions located on B sites due to the dependence of the supertransferred HF on the number of Fe^{3+}(A) nearest neighbors could be established. The Mössbauer spectra taken in fields parallel to the gamma-ray direction for x > 0.6 gave evidence for spin canting, the average canting angle increasing with x.

INTRODUCTION

Zinc substitutions in $NiFe_2O_4$, $CoFe_2O_4$, and recently in Fe_3O_4 [1] are known to cause an increase in the magnetization M for low levels of substitution followed by a decrease in magnetization for larger amounts. A similar trend occurs in the case of lithium ferrite, with only Fe^{3+} as magnetic ion[2]. Based on the cation distribution

$$(Zn_x^{2+}Fe_{1-x}^{3+})\,|Li_{0.5-x/2}^{1+}Fe_{1.5+x/2}^{3+}|\,O_4^{2-} \qquad (1)$$

with diamagnetic Zn^{2+} preferentially occupying the A sites, consistent with the neutron diffraction data of Zhilyakov et al.[3], the moment per F.U. has to increase linearly with x as $\mu=(2.5 + 7.5x)\mu_B$ in the case of a simple Neel colinear spin arrangement.

In the concentration range where the magnetization decreases (x>0.4), large values of the high-field susceptibility have been found[2,3] so, that in the case of x = 0.7 for instance, the magnetization increases with about 25% in the 10-80 kOe range[4]. Recently,[5] low temperature maxima in M in the 30-80K range for x>0.4 and weak micromagnetic behavior for x = 0.5 and 0.6 have been found.

It was obious that the decrease of M above x = 0.4 had to be explained by the magnetic dilution of the A sublattice with zinc, and therefore, by the weakening of the exchange interaction between the Fe^{3+}(B) ions and the Fe^{3+}(A)-sublattice, whereas the Fe^{3+}(B)-Fe^{3+}(B) antiferromagnetic exchange interaction had to remain practically unchanged. The Zn induced reduction of the dominant A-B antiferromagnetic interaction had to lead to departures from a parallel alignment of the Fe(B) spins, and therefore, either to spin canting and/or to spin reversals in the Fe^{3+}(B)-sublattice.

The most attractive model is that of the local spin canting (LSC) proposed by Rosencwaig[6] for magnetically diluted garnets. It allows to determine the local canting angles ϕ(x, n) of a B-spin with respect to the magnetization direction for a given value of x and a number of n Zn^{2+} ions as A-nearest neighbors. In the spinel structure, one has 0<n<6 and usually a random distribution of Zn is assumed, so that the probability of a B spin having n of its six A-site neighbors occupied by Zn^{2+} ions can be calculated from the binomial distribution

$$P(x, n) = \binom{6}{n} x^{6-n}(1-x)^n \qquad (2)$$

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Recent attempts to describe the M(x) and M(H) dependes in the frame of the LSC model[4,5] had only partial success. On the other hand, Mössbauer spectroscopy can be a useful tool in finding experimental evidence for spin canting. Young and Smit[7] concluded from their fit to zero-field room-temperature Mössbauer spectra that no significant spin canting occurs in the lithium-zinc ferrites, but merely reversal of the B spins with less than two A site Fe^{3+} nearest neighbors. In the case of the strongly relaxed room-temperature Mössbauer spectra of the compositions with x > 0.4 a lowering of the temperature down to 4.2 K lifted the relaxation and allowed a better fit to a set of lorentzian sextets[8]. In the case of a random distribution of Zn^{2+} over the A-sites, a distribution of hyperfine field values at the Fe(B) sites HF(B) had to be expected, due to the dependence of the supertransferred contribution to HF(B) on the number of Fe^{3+}(A) nearest-neighbors. In fact, Dormann[8] obtained a reasonable fit to his 4.2K Mössbauer data for x < 0.6 assuming the validity of (2) and a distribution of HF(B)-values which led to an average reduction of HF(B) with 11 ± 2 kOe per Zn^{2+} nearest neighbor. However, the occurrence of the HF(B) distribution had not to be considered as evidence for spin canting.

In order to look for such an evidence, we have undertaken a Mössbauer study of the lithium-zinc ferrites at low temperatures and in the presence of an increasing magnetic field. The obtained results provided evidence for spin canting at least for the compositions with x > 0.6.

EXPERIMENTAL

The samples consisted of hot-pressed Li-Zn ferrites $Li_{0.5-x/2}Zn_xFe_{2.5-x/2}$ with x = 0.0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8. The Mössbauer spectra were taken with a conventional Mössbauer spectrometer with sinusoidal-motion of a Fe/Rh source with an activity of 25mCi. A cryogenic equipment was used in order to allow measurements in the temperature range 4.2-300 K and in a superconducting coil in magnetic fields up to 70 kOe applied in the gamma-ray direction.

RESULTS AND DISCUSSIONS

The Mössbauer spectra of the compositions with x<0.5 taken at 300 and 4.2K showed an increasing tendency to broadening and asymmetrization of the Fe(B)-subspectrum. On the other hand, with the increase of x, especially above 0.5, the Mössbauer spectra exhibited a tendency to strong relaxation, not only at the room temperature which even for x = 0.7 lies much lower than its Curie temperature T_C of 479K, but even at 4.2K. Especially the spectra of the compositions with x = 0.7 and 0.8 (T_C = 238K) show that at 4.2K strong relaxation effects occur. The presence of spin canting can be tested by applying an external field. The field has to align the electronic and nuclear spins in the γ-ray direction, and therefore, due to the anisotropic charater of the γ-absorption (or emission) to lead to the disappearance of the lines 2 and 5 of the Mössbauer ^{57}Fe-sextet which corresponds to the transitions $\Delta m_I = 0$. The persistence of these two lines can be interpreted as evidence for a non-zero spin component perpendicular to the gamma-ray direction and therefore spin canting. Evidence for spin canting has been found for x>0.6 as can be shown in Fig. 1 and Fig. 2 for x = 0.6 and x = 0.7, even when a field of 5 kOe was large enough in order to suppress the effects of the fast

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relaxation. The relative intensities of the lines 2 and 5 are stronger for x = 0.7 and even in a field of 30 kOe they do not disappear completely.

The asymmetric broadened Fe(B)-lines can be taken as evidence for the occurrence of Fe(B) hyperfine field distributions as has been previously assumed by Young and Smit[7] and Dormann[8] owing to the dependence of the Fe^{3+}(B) supertransferred HF on the number of Zn^{2+}(A) nearest neighbors.

In an ideal model, one had to fit the spectra with a set of Fe^{3+}(B)-sextets with relative intensities given by (2) and to determine the experimental canting angles $\phi(x, n)$ from the ratios of the areas A_2, A_5 of the second or fifth, and A_1, A_6 of the first or sixth line of the various spectra using the formula

$$\phi = \arcsin\{(3/2)(A_{2,5}/A_{1,6})/[1 + (3/4)(A_{2,5}/A_{1,6})]\}^{1/2} \quad (3)$$

Unfortunately, no fit in reasonable agreement with this model has been obtained. On the other hand, it was obvious that the spectra taken in higher fields could be fitted reasonably well with Lorentzian quartets with equal linewidth (0.5-0.7 mm/s). In such a way, we obtained the high field fits shown in Fig. 1 and 2. In order to take into account the spin canting effects at lower values of the magnetic field, the corresponding spectra were fitted to Lorentzian sextets (Fig. 1 and 2). This type of fitting procedure led for instance to one Fe(A) and four Fe(B) quartets for x = 0.7 in a field of 70 kOe with the HF values and relative intensities (normalized to unity) given in Table 1. One can notice that the relative intensity of 0.236 of the Fe(A)-subspectrum is much higher than that of 0.140 based on the cation distribution given by (1). This difference can be due to the presence of reversed Fe(B) spins which give rise to an extra contribution to that part of the Mössbauer spectrum where the outer field adds to the hyperfine field, as is usually the case with the Fe(A)-ions.

The fitting to only four Fe(B) sextets is a general consequence of the low values of the probabilities given by the binomial distribution for n = 0, 1, and 2 at high Zn concentrations as x = 0.7. It is reasonable to assume that despite the poor agreement of the relative intensities I/I_o with the probabilities of the binomial distribution (2), B_1, B_2, B_3, and B_4 corresponds to groups of Fe^{3+}(B) ions with 3, 4, 5, and 6 nearest neighbors Zn^{2+} ions on A-sites.

In order to find the average canting angles $\phi(x)$, we have substracted the Fe(A) subspectra from those taken in fields up to 15 kOe and fitted the remaining intensity distribution with a Lorentzian sextet. Then, using the formula (3), $\phi(x)$ values of 38° and 49° in fields of 5 kOe have been found for x = 0.6 and 0.7, respectively. With $\phi(0.7) = 49°$, the value of the magnetic moment/F.U. reaches a too high a value of $4.56\mu_B$ compared to the experimental one of about $2.8\mu_B$ (at 20 kOe).

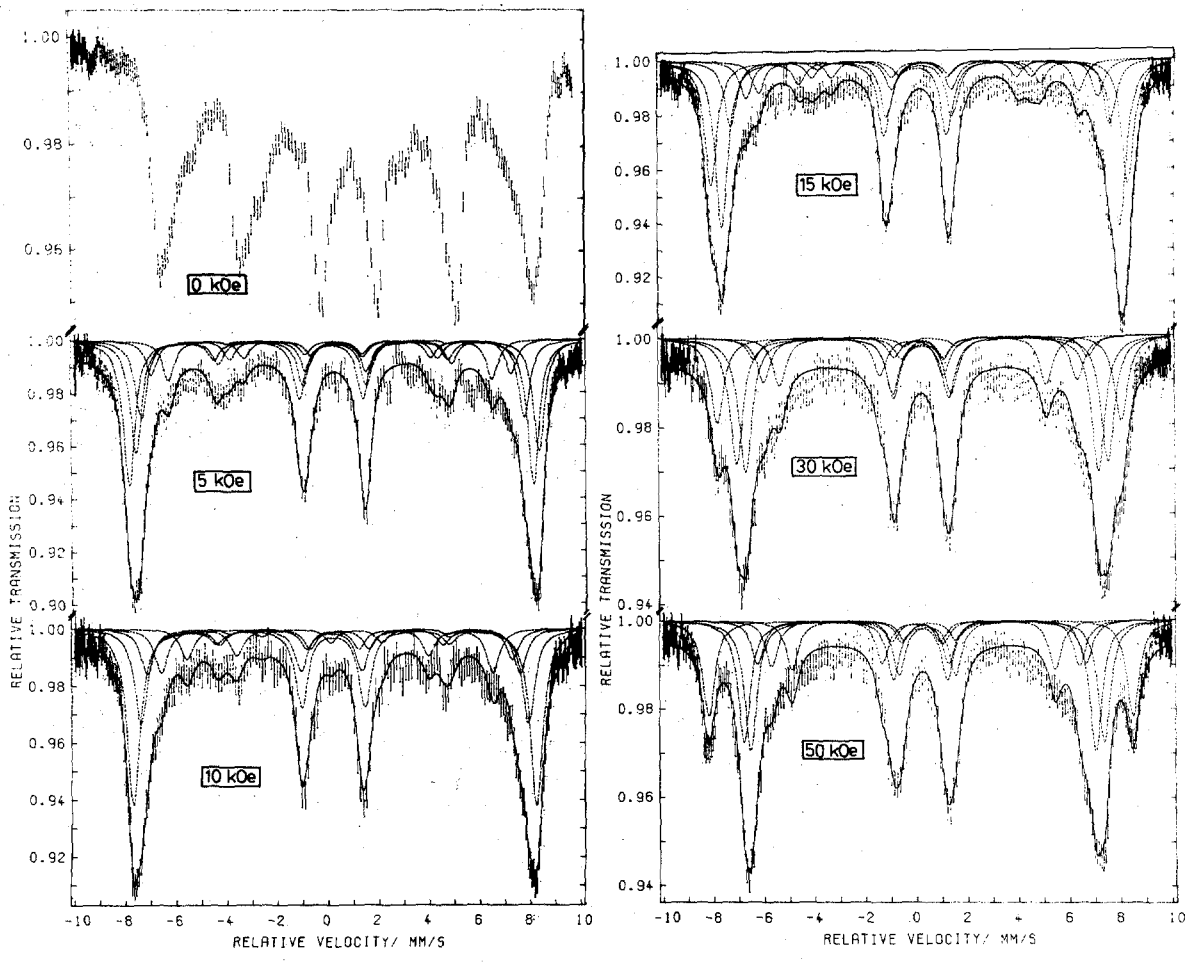

FIG. 1

Mössbauer spectra of Li-Zn ferrite with x = 0.6 at 4.2K in fields up to 50 kOe. Slightly relaxed spectrum in zero field and evidence for spin canting in low fields only (up to about 15 kOe).

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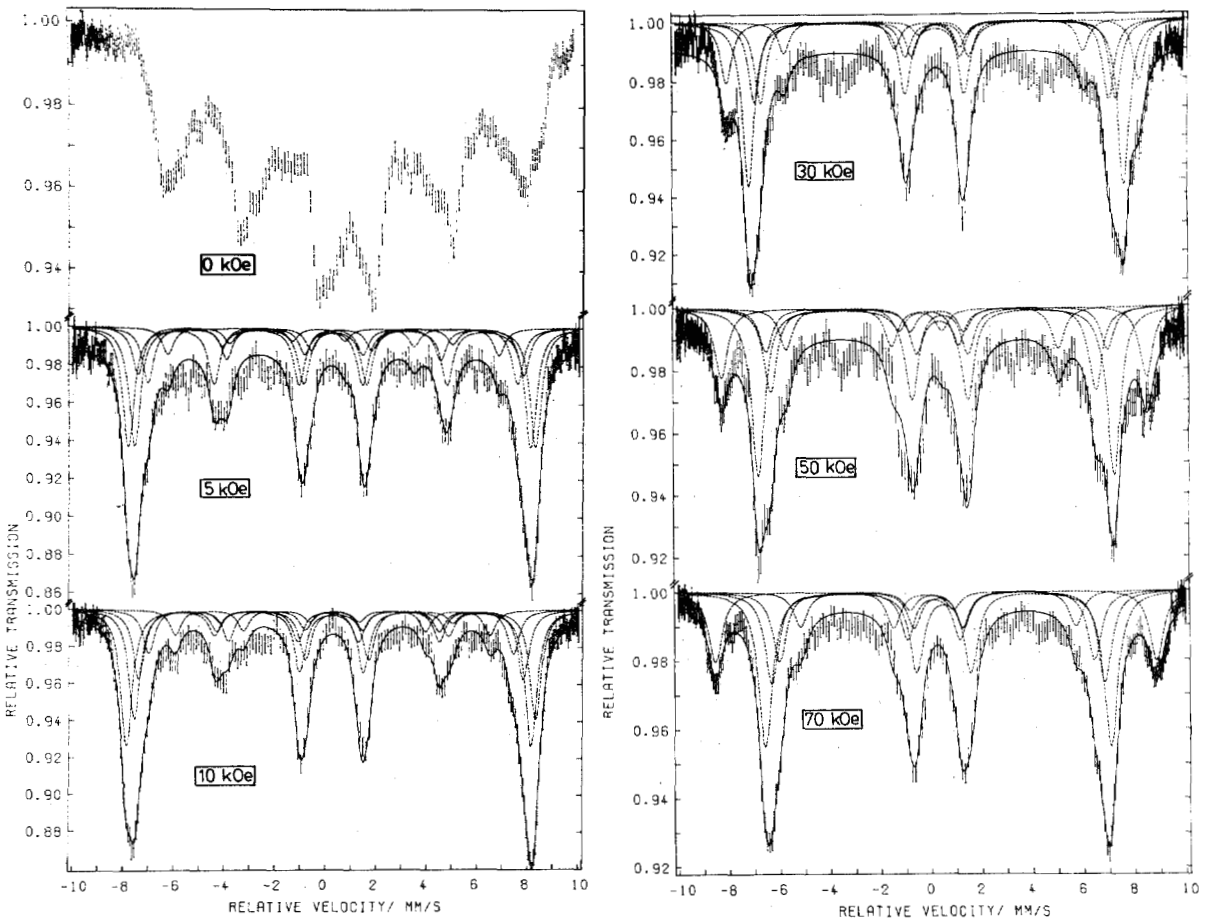

FIG. 2

Mössbauer spectra of Li-Zn ferrite with x = 0.7 at 4.2K in fields up to 70 kOe. Relaxed spectrum in zero field and good evidence for spin canting in fields up to at least 30 kOe.

According to [4], the magnetization changes by about 15% in the field range 20-50 kOe. On the other hand, there is no more Mössbauer evidence for spin canting in a field of 50 kOe for x = 0.7. Therefore, in order to explain the low value of the magnetic moment and its field dependence, one has to assume that besides angles smaller than 90°, a given amount of flipped Fe^{3+}(B) spins has also to be present.

CONCLUSIONS

The study of Mössbauer spectra of LiZn-ferrites at 4.2K in magnetic fields allowed us to find evidence for spin canting for x > 0.6. However, there is no satisfactory agreement between the results of the analysis of the Mössbauer data and those of the magnetic measurements. The presence of a relatively high amount of Fe(B) reversed spins is necessary in order to explain the low values of the magnetization even after the suppression of the spin canting in the outer field.

TABLE I

Hyperfine fields HF and relative intensities I/I_o of the Mössbauer fitting subspectra for x = 0.7.

	A	B_1	B_2	B_3	B_4
HF(kOe)	508	523	507	484	431
I/I_o	0.236	0.346	0.185	0.150	0.083

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